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Supporting Information for

Injectable Highly Loaded Cellulose Nanocrystal Fibers and Composites

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Materials

Freeze-dried cellulose nanocrystals CNCs were purchased from the Process Development Center at the University of Maine. High molecular weight PEO ($M_n = 1000000$ g/mol) and cellulose acetate butyrate (CAB) were purchased from Sigma Aldrich. (Dorset, UK) and was used as received.

Methods:

5 wt.% PEO/water solution and 8 wt.% CNC/water solution was mixed together in a ratio of 1:3 v/v. A 5ml syringe with a needle (gauge= $18\frac{1}{2}$) was used for injection of CNC/PEO solution to acetone. The injection speed was approx. 2mm/sec. The fibers were air dried for at least for two weeks before using for further experiments. Same procedure was followed for manufacturing CNC/CAB composites with the injection of CNC/water 8 wt.% solution was made to 5 wt.% CAB/acetone solution.

Raman spectroscopy

A Renishaw 1000 Raman spectrometer with an imaging microscope equipped with a thermoelectrically cooled CCD detector was utilized to record spectra. A near-IR laser with a

wavelength of 785 nm was used to record spectra from CNC fibers using an exposure time of 30 s and two accumulations. The laser beam was focused using a 50x objective lens to a spot size of $\sim 1\text{-}2\text{ }\mu\text{m}$. To obtain molecular orientation profiles a single fiber was placed with its major axis parallel to the polarization direction of the laser, under the microscope of the Raman spectrometer. At the beginning, both incident and scattered light radiation was polarized parallel to the principle axis of the Raman spectrometer and the major axis of the fiber. Thereafter, the polarization direction of the incident light was changed incrementally using a half-wave plate, and the polarization direction of scattered light was maintained parallel to the fiber axis by using a fixed polarizer. The intensity of a characteristic Raman band located at $\sim 1095\text{ cm}^{-1}$ was recorded as a function of the rotation angle of the incoming polarizer with respect to the axis of the fibers. The maximum intensity was determined from the most intense peak from which a normalization of other intensities was performed.

Fibers were mounted on tensile testing cards for deformation experiments under Raman spectrometer. Samples were deformed in tension using a Deben deformation rig equipped with a 20 N load cell. This deformation rig was carefully placed onto the stage of a Leica microscope, which is connected to the Raman spectrometer. Both the incident and scattered light were polarized parallel to the principle axis of the fibers. The precise positions of the Raman band initially located at $\sim 1095\text{ cm}^{-1}$ were recorded as a function of the tensile strain of the fibers. A Lorentzian function was used to fit the Raman peaks in order to locate their positions, and intensities.

Tensile testing

Fibers were mounted on tensile testing cards for deformation experiments using a Deben deformation rig equipped with a 20 N load cell. The composite samples were deformed at an elongation rate of 0.5 mm/min until tensile failure.

Rheological Characterization

Rheological characterization was performed on a Texas Instruments Rheometer. A cone plate with a diameter of 40 mm and an angle of 3.989° was used. Gap between the plates was maintained at 97 μm . Oscillation frequency experiments were performed at 1% strain in angular frequency range of 0.4 – 100 rad/s. Flow sweep experiments were performed in the shear rate range of 0.0001 to 100 1/s with an equilibration time of 5 s.

Results:

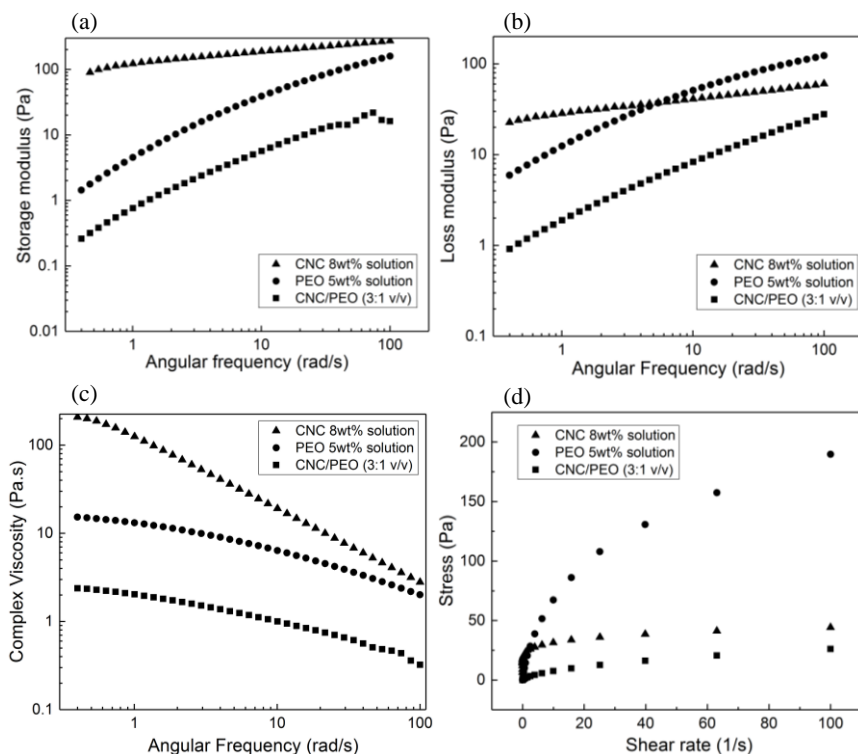


Figure S1. Rheological characterization of CNC and PEO solution (a) storage modulus, (b) loss modulus and (c) complex viscosity as a function of angular frequency, (d) stress vs. shear rate curves.

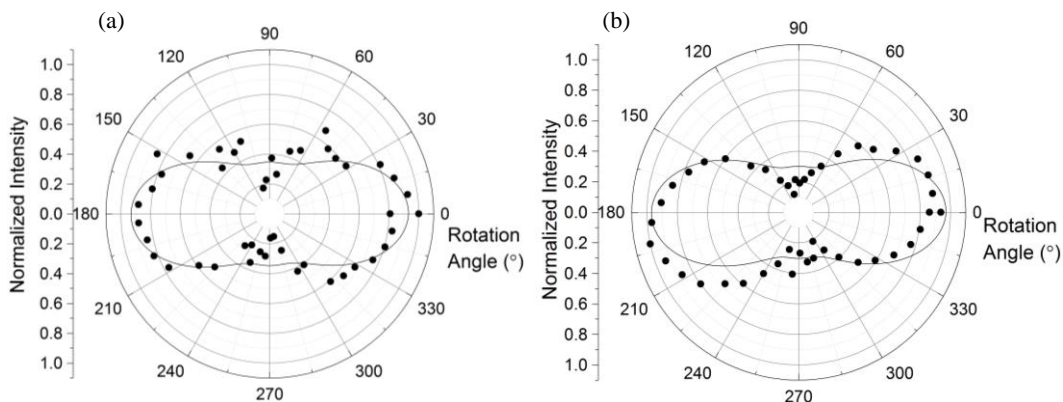


Figure S2. Raman orientation maps of (a) CNC/PAA (poly (acrylic acid)) fibers and (b) CNC/PVA (poly (vinyl alcohol)) fibers injected to acetone. The polar plots were fitted with the equation $I = r + t \cos^4\theta$ where r and t are fitting parameters and θ is the rotation angle and I is the intensity.

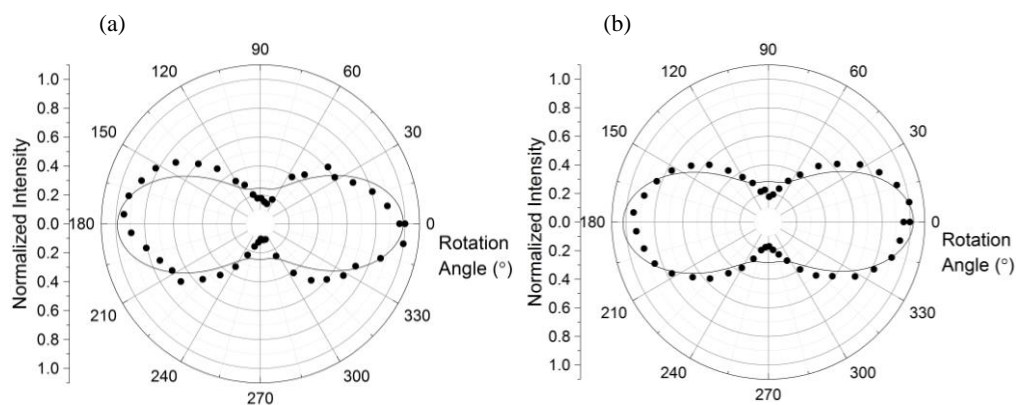


Figure S3. Raman orientation maps of (a) CNC/PEO with 62 wt% CNC loading and (b) CNC/PEO with 76 wt% CNC loading. The polar plots were fitted with the equation $I = r + t \cos^4\theta$ where r and t are fitting parameters and θ is the rotation angle and I is the intensity.

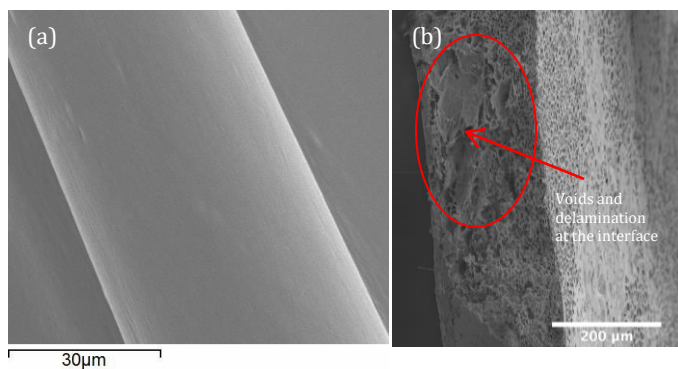


Figure S4. SEM images of (a) CNC/PEO fiber showing a smooth surface, (b) cross-section of a CNC/CAB composite film showing the voids and delamination at the interface after tensile failure.

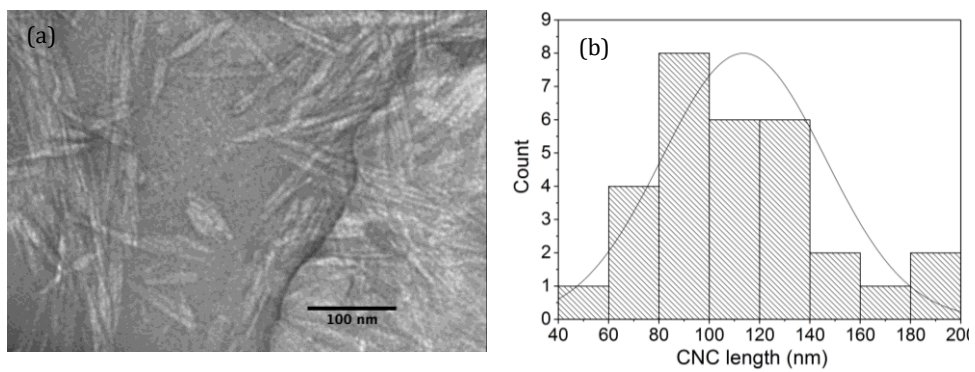


Figure S5. (a) TEM image of CNCs used for manufacturing CNC fibers and (b) histogram showing the measured length of CNCs.